REMARKS

Applicants have amended the claims in order to more particularly define the invention taking into consideration the outstanding Official Action. Applicants most respectfully submit that all of the claims now present in the application are in full compliance with 35 U.S.C. 112 and are clearly patentable over the references of record.

The rejection of claims 30-49 under 35 U.S.C. § 112, second paragraph as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention has been carefully considered but is most respectfully traversed in view of the amendments to the claims. Entry of the amendment is in order to at least place the application in better condition for appeal.

As correctly noted by the Examiner, claims 30 and 40 contain a typographical error in including the word "fix" in the definition of the ring substituent. The word "fix" should read "six" as would be appreciated by one of ordinary skill in the art and as noted by the Examiner in the Official Action. The necessary amendments have been made to each claim to obviate this rejection. Accordingly, it is most respectfully requested that this aspect of the rejection be withdrawn.

Applicants note the Examiner's comments with respect to claims 33, 38, 43 and 48. The Examiner's position is correct. The lack of antecedent basis resulted from an error in the dependency of the claim as also would be appreciated by one of ordinary skill in the art to which the invention pertains. The dependencies for these claims have been corrected to provide proper antecedent basis for the claimed subject matter. Accordingly, it is most respectfully requested that the rejection of these claims for lack of proper antecedent basis be withdrawn. Applicants most respectfully submit that all of the claims now present in the application are in full compliance with 35 USC 112 and are clearly patentable over the references of record.

The rejection of claims 30-49 under 35 U.S.C. § 103 as being unpatentable over Liao et al. combined with Cho et al. and Sato et al. has been carefully considered but is most respectfully traversed. Applicants note the Examiner's comments with respect to the finality of the rejection and have reviewed the cited portion of the MPEP § 706.07(a) but believe that the amendments previously made by applicants, were expected amendments and the present official action should not be final.

In any case, applicants most respectfully submit that all the claims now present in the application are in full compliance with 35 U.S.C. § 112 and clearly patentable over the references of record.

Applicant basically concur with the statements in the official action concerning the teachings of the Liao et al. '087 reference. As stated at column 2 line 3 of the patent, the formula of the cyanine of the invention is shown as a structural formula I. The only variable in this formula is the value of n which represents an integer of 1 and 2. Thus, it would be appreciated by one of ordinary skill in the art that the R substituents must be identical and this is necessary to obtain the results of the invention. There is absolutely no suggestion or motivation in this reference to suggest the modification of the R substituents with the expectation of obtaining the results achieved in the Liao et al. reference much less the improvements obtained by the presently claimed invention. Such a modification is contrary to the clear teaching of the reference.

The teachings of the secondary reference to Cho et al. which includes as counterions TCNQ has been carefully considered. The counterion set forth in the primary Liao et al reference, X^-, represents an acid anion which is preferably a halogen anion, alkylsulfate anion, arylsulfonate anion or a perchlorate anion to provide a cyanine which is thermally stable and soluble in various organic solvents. The Cho et al.

reference relates to an optical recording medium comprising a TCNQ charge transfer complex having an organic electron donor form from a cyanine-based dye shown by formula (I). When the optical recording medium is irradiated with a laser beam, the cyanine-TCNQ in the recording layer absorbs the laser beam and is melted or decomposed thus recording information. Reproduction can be accomplished by reading the reflectivity difference between the recording portion and the non-recording portion with lower power than the recording laser.

In the formula (I) of Cho et al., R represents a heteroaromatic residue and R' represents alkyl; n represents a positive integer not less than 2. Clearly, one of ordinary skill in the art would appreciate the unequivocal teaching in Cho et al that n must be at least 2 and R' alkyl. Therefore, one of ordinary skill in the art would not combine the teachings of Liao et al and Cho et al to arrive at the presently claimed composition as the necessary motivation to make the modifications is not present, other than in applicant's specification which may not be used as a teaching reference. Clearly, Liao et al. states that the R substituents must be identical and are not alkyl but are methoxycarbonyl benzyl.

In addition, the requirement in Cho is that n represents a positive integer which is not less than 2. This does not include the trimethine compound of formula II in the composition as presently claimed. This is a claim limitation which cannot be ignored. There is simply is no motivation to combine the references and arrive at the presently claimed invention when the teachings of the references are considered in their entirety and as would be interpreted by one of ordinary skill in the art to which the invention pertains.

In the Official Action it is urged that the Sato et al. reference '839 teaches that unsymmetrical indoleneic cyanine dyes have higher solubility and stability. Reference

is made to the abstract. It is further urged that indoleneic and benzoindolenic dyes are described throughout. The addition of stabilizers is disclosed. The addition of various materials to the recording layer is disclosed including polymeric binders, the polymeric binder is held to act as an adhesive/glue. However, none of these teachings overcome the deficiencies of the combination of the primary and the secondary reference nor render obvious the presently claimed invention particularly in view of the unique results achieved by the present invention as is set forth in the exemplication in the present application.

Moreover, applicant point out that the cyanine-TCNQ complex dyes disclosed and claimed in the present application had better photostability than the components disclosed in the Liao et al. '087 patent. The test data of the cyanine-TCNQ disclosed in the present application was reported in the attached article entitled "Quencher Free Optical Recording Materials: Photofading Experimental and Anti-Photofading Mechanism Studies". This is further evidence of the results achieved by the presently claimed invention.

For the above reasons, a combination of the Liao et al., Cho et al. and Sato et al. references as set forth in item 5 on page 3 of the Official Action do not render the presently claimed invention *prima facie* obvious since the necessary modifications are not found in the references and applicant's specification may not be used as a teaching reference to combine the references and obtain the presently claimed invention. This is especially true in view of the results achieved by the presently claimed invention already of record, as set forth in the specification and is attached hereto.

In addition, Applicants again wish to note the background of inventor Liao. The inventor, Wen-Yih Liao who is a leader in the department of the data storage media technology, had worked in Industrial Technology Research Institute for 23 years and

describes the conditions for experiments conducted and which it is believed establishes the patentability of the claimed invention as requested by the Examiner.

Condition for technology in the invention

1. The equipments are conventional.

2. The use of temperature as reference to experimentals at page 10~18 of description.

3. How to progress as following

mixing a cyanine-TCNQ dye and an appropriate solvent as a TFP applied on a disk with a weight percent of 1.5%~2.2% under the basis of solute/solution and then;

coating rotationally a mixture of the cyanine-TCNQ dye and the TFP on an unused plastic film by the use of an optical measurement system as ETA-RT (STEAG) to measure a wavelength on a plurality of refractive index as n+ik, wherein said the process respectably relates to a absorption of the dye

4. Relative to experimental data between prior art and the invention

Providing a comparison between prior art (Morishima et al.) and the invention following the sheet; and where k is an absorption coefficient:

TERM	n+ik (658nm) of Dye-X (Prior Art)	n+ik (658nm) of Dye-TCNQ (Invention)
L-type Cyanine	2.383+0.047 i (S0363-ClO4)->benefit	2.150+0.098 i (L-E03-TCNQ)->benefit
SL-type Cyanine	2.104+0.015 i (SL-PF6)->benefit	2.090+0.045 i (SL-TCNQ)->benefit
S-type Cyanine	2.210+0.015 i (S-PF6)->benefit	1.980+0.040 i (S-E03-TCNQ)->benefit

As a conclusion, with respect to said the data combinations, a higher solubility of the invention with Cyanine dye-TCNQ complex is better then the Morishima's, which the solubility of the invention is 32 wt% and the solubility of the Morishima isn't higher 0.5 wt% and, could be equal to 0.5 wt%.

Note: Reference to experimental examples at page 10~18, of description, which had been stated the details.

In the Official Action, on page 5, it is urged that the Liao reference teaches mixtures of pentamethine and trimethine indolene cyanine dyes bearing methyl esters of 4-benzoic acid substituents in appropriate ratios for recording. It is then stated that the use of the methyl ester 4-benzoic substituent is disclosed as resulting in gains in solubility and thermal stability. However, as previously noted by applicants, it is a requirement of the reference, as would be appreciated by one of ordinary skill in the art that both R substituents contain the 4-benzoic acid substituents and there is no suggestion to remove one of the substituents in accordance with the presently claimed invention.

The statement that the Sato et al. reference teaches that changing one of the end substituents to make dyes less structurally similar is old and the resulting increase in solubility well known in the art. This is clearly hindsight reconstruction based upon applicant's specification. One of ordinary skill in the art would not interpret the references, in their entirety, to make the necessary selection to arrive at the presently claimed invention. Accordingly, it is most respectfully requested that this rejection be withdrawn.

Applicants note the examiner's comments with respect to the data present and believe that applicant's invention is clearly patentable in that a *prima facie* case of obviousness has not been established by the rejection for the above reasons. Clearly, the testing and information presented, including those in the attached Journal article must be taken into consideration and given some weight and clearly evidence the advantages of the presently claimed invention. Accordingly, it is most respectfully requested that this rejection be withdrawn.

The rejection of claims 39-40 under 35 U.S.C. § 103(a) being unpatentable over Liao et al. ('087, combined with Cho et al. and Sato et al.) and further in view of Ishida et al. has been considered but is most respectfully traversed for the above reasons.

The Ishida et al. reference is stated to teach the dyes of formula I mixed with TCNQ compounds A1 or A2. It is stated that the use of a recording layer having thickness of 50 to 300 nm is disclosed. The use of various metals such as the preferred gold, silver, aluminum, copper or chromium alloys is suggested. However, none of these teachings overcome the deficiencies in the initial combination of the references and for the above reasons, it is most respectfully requested that this rejection be withdrawn.

In view of the above comments and further amendments to the claims, favorable reconsideration and allowance of all the claims now present in the application are most respectfully requested.

Respectfully submitted,

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Quencher-Free Optical Recording Materials: Photofading Experimental and Antiphotofading Mechanism Studies

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In the experiment of antiphotofading of DVD-R optical recording disc, a 3000 W xenon light ($\lambda = 420$ nm) was adopted for testing the parameters of a novel cyanine-TCNQ (tetracyanoquinodimethane) charge transfer complex as a recording layer. Its performance without addition of a singlet oxygen quencher under illumination of 1200 min still satisfies with the DVD-R media requirements (3T CNR $\geq$ 45 dB; Reflectance $\geq$ 45%). Improved photostability in this modified cyanine dye is explained by a two-step photoinduced electron transfer (2-step PET) process between intramolecular Donor (Cyanine)–Acceptor (TCNQ) couple. [DOI: 10.1143/JJAP.42.3447]

KEYWORDS: antiphotofading, 3T CNR, two-step photoinduced electron transfer (two-step PET), CD-R, DVD-R, TCNQ

1. Introduction

Cyanine dyes are generally accepted as the most consumed organic optical recording media in CD-R and DVD-R production. However, one of its drawbacks is poor photostability (or antiphotofading) property. Carbocyanine was the first material applied to optical disc recording formulation by Law et al.,[1] but it has been considered a commercial failure. Various modifications have been investigated worldwide. Yanagisawa et al.[2] added quenchers into the formulation to improve photostability. Morishima et al.[3] found that doping neutral TCNQ (7,7,8,8-tetracyanoquinodimethane) derivative in cyanine improved the antiphotofading property significantly. Neutral TCNQ is not quite soluble in common organic solvents making the content of doping dye formulation limited. The stability is also limited. Using EPR and H-NMR analyses, Wu et al.[4] found that squarylium cyanine molecule produces free electron in the resonance carbon chain easily when it is excited by light. The reaction of free electron and O_2 leads to a series of decomposition reactions.

In this study, simple salts, cyanine-TCNQ complexes with 1 : 1 mole ratio, were used in the recording layer. The TCNQ electrostatically binds to cyanine dye molecule through the charge transfer process. Further, this Cyanine-TCNQ complex was evaluated by a photostability test under 3000 W Xe lamp excitation. Its performance as a qualified optical recording layer must meet all the requirements of DVD media. 3T CNR is one of the strict performance tests used to examine the requirements. Based on spectra and cyclic voltammetry (C–V) analyses, we propose a novel mechanism to explain its improved photostability.

2. Materials and Methods

Simple salts, cyanine-TCNQ complexes, were prepared by the method of Lupinski[5] and Hu et al.[5] In this investigation, we intend to combine the TCNQ and the cyanine dye to form an intramolecular charge transfer complex (cyanine-TCNQ complex), the structure of which, as shown in Fig. 1, possesses good solubility in organic solvents.

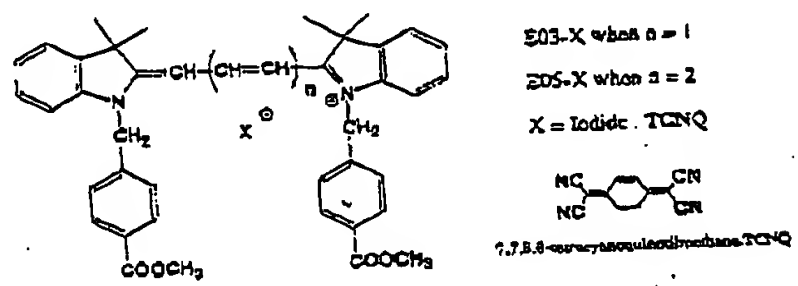

Fig. 1. Structure of the cyanine dyes.

In order to improve the performance of DVD-R, we take the mixture of E03-X and E05-X (X denotes the counter-ion, Iodide or TCNQ). Actually, the formulation is a common practice. Five different samples labeled components I–V are prepared. Component I consists of a mixture of E03-Iodide and E05-Iodide; component II consists of a mixture of E03-TCNQ and E05-Iodide; component III consists of a mixture of E03-TCNQ and E05-TCNQ; component IV consists of a mixture of commercial cyanine dyes; and component V consists of a mixture of commercial cyanine dyes and commercial quencher. The commercial cyanine dyes consist of OM78 and OM79 (Fuji Photo Film Co. Ltd. Japan). The commercial quencher consists of Q01 (NKSK, Japan). All were dissolved in TFPA (2,2,3,3-tetrafluoropropanol) separately to make a 3g dye solution for spin coating onto DVD-R blank substrate using a spin coater (Steag Microtech). The thickness of the coating was about 500–2000 Å. It was then sputtered with a layer of Ag to form a reflection layer of 500–1000 Å thickness. Finally, the combination of one substrate plate sputtered with a reflection layer and a high-density recording layer, and blank substrate plate high-density optical recording disc for investigation.

Weather-Ometer (ATLAS Ci400) provides a 3000 W xenon lamp to irradiate high intensity light at 420 nm to test the photofading of the organic recording layer. The reflectivity and 3T CNR of the optical disc with different irradiation durations were determined using optical density spectrometer (ETA-OD) and Pulstec DDU 1000, respectively.

In order to evaluate the electron transfer between cyanine-TCNQ intramolecular charge transfer complex under light irradiation, the energy levels of molecular orbitals (HOMO,

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Table I. Photofading test (I) of DVD-R disc.

Recording layer	Reflectivity (%) measurements under laser of $\lambda = 635$ nm						
	Exposure time to Xe lamp (3000 W, $\lambda = 420$ nm)						
	0 min	30 min	90 min	150 min	780 min	960 min	1200 min
Component I	65.8	63.0	<45%				
Component II	53.2	62.8	54.3	45.4	<45%		
Component III	48.6	48.6	48.6	48.6	48.5	48.3	45.8
Component IV	79.0	72.7	68.5	<45%			
Component V	74.0	72.7	69.7	69.2	<45%		

Table II. Photofading test (II) of DVD-R disc.

Recording layer	3T CNR measurements under laser of $\lambda = 635$ nm, writing power 11 Mw						
	Exposure time to Xe lamp (3000 W, $\lambda = 420$ nm)						
	0 min	30 min	90 min	150 min	780 min	960 min	1200 min
Component I	56.0	<45 dB					
Component II	57.2	50.4	<45 dB				
Component III	55.9	54.2	54.3	54.2	54.5	53.6	50.8
Component IV	57.2	52.4	48.2	<45 dB			
Component V	56.3	56.5	55.4	52.0	<45 dB		

LUMO) were determined by evaluating its optical and redox properties.[7] Optical properties of dyes were evaluated as follows: Dye concentration was varied from 9.47×10^{-7} to 4.91×10^{-6} mol/l, and ethanol was used as a solvent. Absorption and fluorescence spectra of cyanine dyes and neutral TCNQ were recorded using ultraviolet spectroscopy (Hitachi U-3500) and fluorescence spectrum (Hitachi F-2500), respectively. Quantum yields of fluorescence (Φ_{FL}) were determined according to the method of Parker[8] using Rose Bengal as reference ($\Phi_{FL} = 0.14$). Redox properties of dyes were measured according to the method of Lenhard and Cameron.[9] Acetonitrile, further purified and dewatered,[10] was used as the solvent containing 0.1 M TBA-BF_4 (Tetrabutylammonium tetrafluoroborate) as electrolyte.

3. Results and Discussion

3.1 Absorption in optical recording materials

From UV-Vis spectra of the optical disc shown in Fig. 2, we clearly see that the dye film of component II and component III, which consist of Cyanine-TCNQ complex,

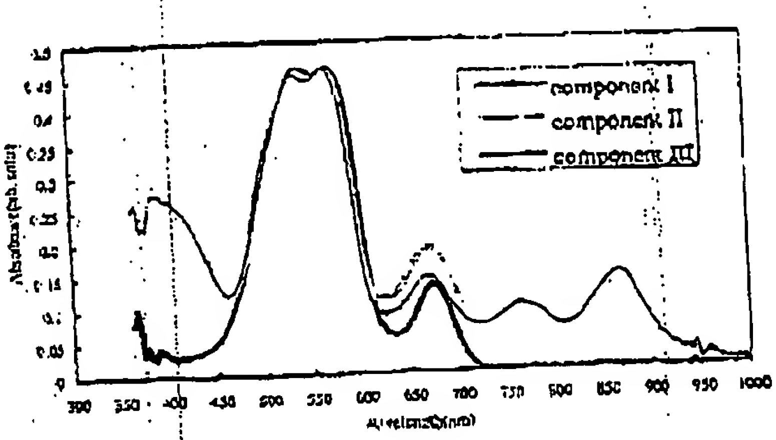

Fig. 2. Absorption spectra of three different components: components I, II, III.

have two special absorption peaks at wavelengths at about 760 nm and 860 nm. Thus they are slightly red-shifted from the absorption peaks of dye solution (which is at about 740 nm and 840 nm). These two special absorption peaks arise from the distinctive charge transfer absorption peak that appears in forming the TCNQ complex.[5,11] Furthermore, the absorption at the wavelength of 350–450 nm is the absorption of TCNQ itself in cyanine-TCNQ complex.[5] The above-mentioned peaks do not appear in component I.

3.2 Reflectivity and 3T CNR studies

The data exhibited in Tables I and II are the photofading measurements of optical discs consisting of five different samples as recording layer. From the results in Tables I and II, we find that along with the increment of TCNQ proportion in recording layer, its corresponding antiphotofading performance improved; but relatively, the reflectivity of optical disc under laser of $\lambda = 635$ nm before being exposed to xenon light decreased with the increment of TCNQ proportion. This phenomenon arose from the increment of the k value in the refractive index $(n + ik)$ of recording layer with different compositions at wavelength 635 nm. The k value increases with the increasing TCNQ proportion (see Table III), while the n value decreases. As a result, absorptivity of the optical disc increases, and reflectivity decreases at wavelength 635 nm.[12]

Table III. Refractivity of DVD-R disc.

Recording layer	Refractivity $(n + ik)$ under laser of $\lambda = 635$ nm
Component I	$2.151 + 0.046i$
Component II	$2.143 + 0.100i$
Component III	$2.108 + 0.135i$
Component IV	$2.300 + 0.032i$
Component V	$2.253 + 0.051i$

Table VI. Energy levels of cyanine-TCNQ complex: E_{CTL1}, E_{CTL2}.

Compound	E_{HOMO} ($TCNQ^-$ in Cyanine)	$\lambda_{CT1,max}$(nm)	E_g(eV) $\lambda = \lambda_{CT1,max}$	E_{CTL1} (eV)	E_{LUMO} ($TCNQ^-$ in Cyanine)
E03-TCNQ	−7.106	743	1.67	−5.436	−4.152
E05-TCNQ	−7.125	744	1.66	−5.465	−3.811
Compound	E_{HOMO} ($TCNQ^-$ in Cyanine)	$\lambda_{CT2,max}$(nm)	E_g(eV) $\lambda = \lambda_{CT2,max}$	E_{CTL2} (eV)	E_{LUMO} ($TCNQ^-$ in Cyanine)
E03-TCNQ	−7.106	841	1.48	−5.626	−4.152
E05-TCNQ	−7.125	841	1.48	−5.645	−3.811

From Table II, the reflectivity of component III remains 50% or more even after 1200 min of exposure to 3000 W Xe lamp excitation, and it still fulfills the requirement of DVD-R media (3T CNR ≧ 45 dB, reflectivity ≧ 45%), while the reflectivity values of those of component IV and component V containing commercial cyanine dye with or without commercial quencher added are less than the 45%. This indicates that the charge transfer complex in formulation is a correct choice for improving performance.

3.3 *Antiphotofading mechanism of cyanine-TCNQ complex: 2-step photoinduced electron transfer process (2-step PET)*

According to the following equations proposed by Dähne.[7]

$$E_{LUMO} = EA = -4.42 - E_{Red} \quad (\text{V vs. Ag/AgCl SCE}) \quad (1)$$

$$E_{HOMO} = IP = -E_{LUMO} - E_{\lambda max} \quad (\text{eV}) \quad (2)$$

$$E_{\lambda max} = \frac{hc}{\lambda_{max}} = \frac{1240.82397}{\lambda_{max}} \quad (\text{eV}), \quad (3)$$

the energy levels of the lowest unoccupied molecular orbital E_{LUMO} and highest occupied molecular orbital E_{HOMO} of the dye can be calculated from the reduction potential E_{Red} of the dye and the energy $E_{\lambda max}$ (eV) (Table IV), which corresponds to the wavelength of maximum absorption of the dye. For the convenience, we divide the molecular orbital of cyanine-TCNQ complex into the main structure of cyanine$^+$ carrying positive charge, and $TCNQ^-$ carrying negative charge. The calculated values for the dye are given in Table IV. Comparing the HOMO orbitals of cyanine$^+$ and $TCNQ^-$ in cyanine-TCNQ complex, we found that the HOMO energy level of $TCNQ^-$ was relatively low, i.e., its electron affinity (EA) was high. This result also confirms the general electron acceptor role of TCNQ in cyanine-TCNQ complex.

Table IV. Measured redox potentials and calculated energy levels of E_{HOMO}, E_{LUMO} by eqns. (1), (2) and (3).

Compound[a]	$E_{reduction}$ (V)	$E_{oxidation}$ (V)	λ_{max} (nm)	E_{HOMO} (eV)	E_{LUMO} (eV)
E03-I	−0.682	0.339	553	−5.981	−3.738
$E03^-$ (in E03-TCNQ)	−0.713	0.344	553	−5.951	−3.707
$TCNQ^-$ (in E03-TCNQ)	−0.268	−0.159	420	−7.106	−4.152
E05-I	−0.6	0.335	549	−5.731	−3.820
$E05^-$ (in E05-TCNQ)	−0.609	0.343	549	−5.722	−3.811
$TCNQ^-$ (in E05-TCNQ)	−0.263	−0.156	418	−7.125	−4.157

a) Solvent: EtoH (HPLC grade)

Table V. UV absorption and fluorescence (FL) emission properties of cyanine dyes.

Dye	E03-I	E03-TCNQ	E05-I	E05-TCNQ	TCNQ
$\lambda_{abs,max}$ (Dye+)[a] (nm)	553	553	649	649	396
$\lambda_{abs,max}$ (TCNQ−)[a] (nm)	nil	420	nil	418	nil
$\lambda_{abs,max}$ (CT1)[a] (nm)	nil	743	nil	744	nil
$\lambda_{abs,max}$ (CT2)[a] (nm)	nil	841	nil	841	nil
λ_{max} (FL)[a] (nm)	574	573	672	671	465,603
$\Phi_{FL}^{b)}$	0.1299	0.1734	0.0274	0.0301	

a) CT, abs and FL denotes charge transfer, absorption and fluorescence, respectively.
b) Reference: Rose Bengal (TCI). $\Phi_{FL} = 0.14$

Table V indicates that there are two stable charge transfer absorption peaks (at about $\lambda = 740$, 840 nm) in the solution of cyanine-TCNQ complex. There are two stable molecular orbitals existing between HOMO and LUMO of TCNQ in the cyanine-TCNQ complex. They are denoted CTL1 and CTL2, respectively. The energy levels of E_{CTL1} and E_{CTL2} were also calculated from eqns. (1), (2) and (3) (as shown in Table VI).

According to data in Tables V and VI we propose the mechanism of 2-step PET to describe the electron transfer process of cyanine-TCNQ complex under light irradiation (see Fig. 3). The 2-step PET process involves a cyclic electron transfer of Step 1, FL, and Step 2 between HOMO.

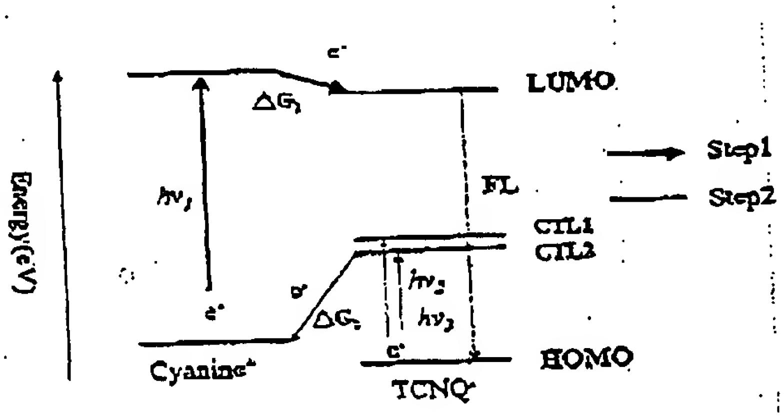

Fig. 3. Two-step photoinduced electron transfer process between intra-molecular donor-acceptor couple: cyanine-TCNQ complex.

LUMO of cyanine$^-$ and TCNQ$^-$, respectively, where Step 1 and Step 2 are PET processes.[13] The PET process of Step 1 includes the electron transfers from the HOMO to LUMO of cyanine$^+$ while the dye is excited by light irradiation ($h\nu_1$). The decrement of IP (i.e., ionization potential) of the electron that jumped to LUMO of cyanine$^-$ increases the driving force of electron transfer from the LUMO of cyanine$^+$ to the LUMO orbital of TCNQ$^-$, and forms the transition state of cyanine^{2-} and TCNQ^{2-}. Free energy change of Step 1 is ΔG_1.

The electron transfer to LUMO orbital of TCNQ$^-$ after going through PET process of Step 1, then returns to HOMO orbital of TCNQ$^-$ by emitting fluorescence (shown in Table V). The PET process of Step 2 includes electron transfer from the HOMO to the CTL1 and CTL2 energy levels of TCNQ$^-$ while the dye is excited by light irradiation ($h\nu_2$, and $h\nu_3$ respectively). This decreases the IP of electron and increases the driving force of electron transfers from the CTL energy level of TCNQ$^-$ to the HOMO orbital of cyanine$^-$. Cyanine-TCNQ dye once again returns to a ground state, which is in cyanine$^+$ and TCNQ$^-$ states. Free energy change of Step 2 is ΔG_2.

Furthermore, the free energy change ΔG_1, ΔG_2 can be calculated by the following simplified Rehm-Weller equation if the excited molecule is the electron donor:[14]

$$\Delta G = [E(D^+/D) - E(A/A^-)] - E^*(\text{eV}) \quad (4)$$

$$= 23.06\{[E(D^+/D) - E(A/A^-)] - E^*\}, \quad (5)$$

where $E(D^+/D)$ is the oxidation potential of the electron donor molecule, $E(A/A^-)$ is the reduction potential of the electron acceptor molecule during the PET process, and E^* is the energy required, when the electron is excited by light from a low to high energy orbital. The calculated values of ΔG_1 and ΔG_2 are given in Tables VII and VIII, respectively.

Since ΔG_1 and ΔG_2 are all negative, we can conclude that the 2-step PET process of cyanine-TCNQ complex is spontaneous and thermodynamical. Therefore, the cyanine-TCNQ complex returns to the ground state immediately while the dye molecule is excited by light.

Table VII. Gibbs free energy change during Step 1 of PET process.

Dye	ΔG_1 (eV)	ΔG_1 (Kcal/mol)	PET
E03-TCNQ	−1.63	−37.58	Spontaneous
E05-TCNQ	−1.30	−30.13	Spontaneous

Table VIII. Gibbs free energy change during Step2 of PET process.

DYE	ΔG_2 (eV)	ΔG_2 (Kcal/mol)	PET
E03-TCNQ ($\lambda_{abs,max}$ = 743 nm)	−1.11	−25.73	Spontaneous
E03-TCNQ ($\lambda_{abs,max}$ = 591 nm)	−0.92	−21.23	Spontaneous
E05-TCNQ ($\lambda_{abs,max}$ = 7[illegible]4 nm)	−1.21	−27.99	Spontaneous
E05-TCNQ ($\lambda_{abs,max}$ = 841 nm)	−1.02	−23.55	Spontaneous

Table IX. Gibbs free energy change of cyanine dyes while O_2 served as electron acceptor (EA) during photoinduced electron transfer.

Dye	ΔG_{O2} (eV)	ΔG_{step1} (eV)
E03-TCNQ	−1.52	−1.63
E03-I	−1.67	nil
E05-TCNQ	−1.17	−1.30
E05-I	−1.12	nil

Under light excitation, oxidation proceeds to induce dye photofading.[4,15] As mentioned above the cyanine-TCNQ complex may return to the ground state immediately through spontaneous 2-step PET under light excitation. Thus the oxidation and the 2-step PET are parallel and competitive reaction in cyanine-TCNQ.

In order to distinguish which reaction dominates, the Gibbs free energy change from cyanine dye to the formation of superoxide radical anion O_2^-, ΔG_{O2},[16] and ΔG_{step1} in step 1 of the 2-step PET process were calculated and listed in Table IX.

From the data of Gibbs free energy change in Table IX, we find that the parallel processes mentioned above are both spontaneous and thermodynamical. The results also reveal that a quencher or antioxidant is not added, and O_2 molecule forms oxides with the excited cyanine molecule through the PET process. Thus photofading of dye molecule is induced and makes the photostability of cyanine dye poor. Furthermore, the absolute values of ΔG_{O2} of cyanine-TCNQ complex are all smaller than ΔG_{step1}, which implies that during step 1 in the 2-step PET process, cyanine-TCNQ is in a favorable position to resist oxidation. Thus, cyanine-TCNQ complex has better resistance against the photofading reaction when the dye is attacked by oxygen while the dye molecule is excited by light.

4. Conclusion

Based on the photofading experiments of xenon light exposure, the optical disc on which these lab-made cyanine-TCNQ complexes without addition of any quencher or lightstabilizer in the formulation served as recording layer has better anti-photofading capability than commercial cyanine dyes with the commercial quencher added which also serve as a recording layer. These charge transfer complexes formed between cyanines and TCNQ rendered better antiphotofading properties owing to the spontaneous 2-step PET process while the dye is excited by light to prevent attacking by oxygen molecule.

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